

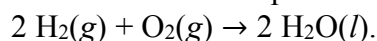
Chemical Kinetics - Reaction Rates

Chemical kinetics is the branch of chemistry which addresses the question: "how fast do reactions go?" Chemistry can be thought of, at the simplest level, as the science that concerns itself with making new substances from other substances. Or, one could say, chemistry is taking molecules apart and putting the atoms and fragments back together to form new molecules. (OK, so once in a while one uses atoms or gets atoms, but that doesn't change the argument.) All of this is to say that chemical reactions are the core of chemistry.

If Chemistry is making new substances out of old substances (i.e., chemical reactions), then there are two basic questions that must be answered:

1. Does the reaction want to go? This is the subject of chemical thermodynamics.
2. If the reaction wants to go, how fast will it go? This is the subject of chemical kinetics.

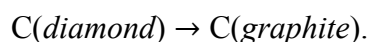
Here are some examples. Consider the reaction,



We can calculate $\Delta_r G^\circ$ for this reaction from tables of free energies of formation (actually this one is just twice the free energy of formation of liquid water). We find that $\Delta_r G^\circ$ for this reaction is very large and negative, which means that the reaction wants to go very strongly. A more scientific way to say this would be to say that the equilibrium constant for this reaction is very very large.

However, we can mix hydrogen gas and oxygen gas together in a bulb or other container, even in their correct stoichiometric proportions, and they will stay there for centuries, perhaps even forever, without reacting. (If we drop in a catalyst - say a tiny piece of platinum - or introduce a spark, or even illuminate the mixture with sufficiently high frequency uv light, or compress and heat the mixture, the mixture will explode.) The problem is not that the reactants do not want to form the products, they do, but they cannot find a "pathway" to get from reactants to products.

Another example: consider the reaction,



If you calculate $\Delta_r G^\circ$ for this reaction from data in the tables of thermodynamic properties you will find once again that it is negative (not very large, but still negative). This result tells us that diamonds are thermodynamically unstable. Yet diamonds are highly regarded as gem stones ("diamonds are forever") and are considered by some financial advisors as a good long-term investment hedge against inflation. On the other hand, if you were to vaporize a diamond in a furnace, under an inert atmosphere, and then condense the vapor, the carbon would come back as graphite and not as diamond.

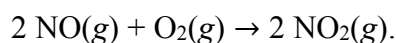
How can all these things be?

The answer is that thermodynamics is not the whole story in chemistry. Not only do we have to know whether a reaction is thermodynamically favored, we also have to know whether the reaction can or will proceed at a finite rate. The study of the rate of reactions is called chemical kinetics.

The study of chemical kinetics requires new definitions, new types of experimental data, and new theories and equations to organize the data. We begin with the definition of *reaction rate*.

Reaction Rates

Consider the reaction,



We can specify the rate of this reaction by telling the rate of change of the partial pressures of one the gases. However, it is convenient to convert these pressures into concentrations, so we will write our rates and rate equations in terms of concentrations, where square brackets, [], mean concentration in mol/L.

We might try to write the rate variously as,

$$\frac{d[\text{NO}_2]}{dt},$$

or as

$$-\frac{d[\text{O}_2]}{dt},$$

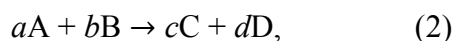
but these are not the same because each molecule of O_2 gives two molecules of NO_2 .

To arrive at an unambiguous definition of reaction rate we define the "reaction velocity," v , as

$$v = \frac{1}{2} \frac{d[\text{NO}_2]}{dt} = -\frac{d[\text{O}_2]}{dt} = -\frac{1}{2} \frac{d[\text{NO}]}{dt}. \quad (1)$$

This is unambiguous. The negative sign tells us that that species is being consumed and the fractions take care of the stoichiometry. Any one of the three derivatives can be used to define the rate of the reaction.

For a general reaction,



the reaction velocity can be written in a number of different but equivalent ways,

$$v = -\frac{1}{a} \frac{d[\text{A}]}{dt} = -\frac{1}{b} \frac{d[\text{B}]}{dt} = \frac{1}{c} \frac{d[\text{C}]}{dt} = \frac{1}{d} \frac{d[\text{D}]}{dt}. \quad (3)$$

As in our previous example, the negative signs account for material that is being consumed in the reaction and the positive signs account for material that is being formed in the reaction. The stoichiometry is preserved by dividing the rate of change of concentration of each substance by its stoichiometric coefficient.

Rate Laws

A rate law is an equation that tells us how fast the reaction proceeds and how the reaction rate depends on the concentrations of the chemical species involved. A rate law is an equation of the form,

$$v = f([\text{A}], [\text{B}], \dots [\text{E}]). \quad (4)$$

Equation 4 gives us a first order differential equation in t because the reaction velocity is related to a time-derivative of one of the concentrations (as in Equation 3).

The rate law may contain substances which are not in the balanced reaction and may not contain some things that are in the balanced equation (even on the reactant side).

Usually rate laws take the form,

$$v = k[A]^x[B]^y[E]^z \dots, \quad (5)$$

where x, y, z , are small whole numbers or simple fractions and k is called the "rate constant." The sum of $x + y + z + \dots$ is called the "order" of the reaction.

Common types of rate laws:

1. First Order Reactions

In a first order reaction the rate is proportional to the concentration of one of the reactants. That is,

$$v = \text{rate} = k[B], \quad (6)$$

where B is a reactant. If we have a reaction which is known to be first order in B, such as

B + other reactants \rightarrow products,

we would write the rate law as,

$$-\frac{d[B]}{dt} = k[B]. \quad (7)$$

The constant, k , in this rate equation is the first order rate constant.

2. Second Order Reactions

In a second order reaction the rate is proportional to concentration squared. For example, possible second order rate laws might be written as

$$\text{Rate} = k[B]^2 \quad (8)$$

or as

$$\text{Rate} = k[A][B]. \quad (9)$$

That is, the rate might be proportional to the square of the concentration of one of the reactants, or it might be proportional to the product of two different concentrations.

3. Third Order Reactions

There are several different ways to write a rate law for a third order reaction. One might have cases where

$$\text{Rate} = k[A]^3, \quad (10)$$

or

$$\text{Rate} = k[A]^2[B], \quad (11)$$

or

$$\text{Rate} = k[A][B][C], \quad (12)$$

and so on.

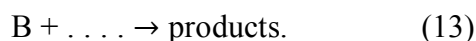
We will see later that there are other, more "interesting" rate laws in nature, but a large fraction of rate laws will fit in one of the above categories.

Integrated forms of rate laws

In order to understand how the concentrations of the species in a chemical reaction change with time it is necessary to integrate the rate law (which is given as the time-derivative of one of the concentrations) to find out how the concentrations change over time.

1. First Order Reactions

Suppose we have a first order reaction of the form,



Then we can write the rate law and integrate it as follows (recall that the derivative is negative because the concentration of the reactant, B, is decreasing):

$$\begin{aligned} \frac{d[B]}{dt} &= -k[B] \\ \frac{d[B]}{[B]} &= -k dt \\ \ln \frac{[B]}{[B]_0} &= -kt \\ [B] &= [B]_0 e^{-kt}. \end{aligned} \quad (14a, b, c, d)$$

The first order rate law is a very important rate law, radioactive decay and many chemical reactions follow this rate law and some of the language of kinetics comes from this law. The form of Equation 14d is called an "exponential decay." This form appears in many places in nature. One of its consequences is that it gives rise to a concept called "half-life."

Half-life

The half-life, usually symbolized by $t_{1/2}$, is the time required for [B] to drop from its initial value $[B]_0$ to $[B]_0/2$.

Using the integrated form of the first order rate law we find that

$$\begin{aligned} \frac{[B]}{2} &= [B]_0 e^{-kt_{1/2}}, \\ \text{or} \\ \frac{1}{2} &= e^{-kt_{1/2}}. \end{aligned} \quad (15a, b)$$

Taking the logarithm of both sides gives,

$$\ln \frac{1}{2} = -k t_{1/2}$$

$$\ln 2 = k t_{1/2}, \quad (16a, b)$$

or

$$t_{1/2} = \frac{\ln 2}{k}. \quad (17)$$

(You can also write

$$[B] = [B]_0 2^{-\frac{t}{t_{1/2}}} = \frac{[B]_0}{2^{\frac{t}{t_{1/2}}}}, \quad (18)$$

which may actually give a little more insight into what is meant by half-life. This equation demonstrates clearly that the concentration drops by a factor of two for every $t_{1/2}$ increment in time.)

For first order processes it is common to define a "relaxation time." τ , by

$$\tau = \frac{1}{k}, \quad (19)$$

so that one can write the integrated form of the rate law as

$$[B] = [B]_0 e^{-t/\tau}. \quad (20)$$

τ is the time required for $[B]$ to drop from $[B]_0$ to $[B]_0/e$. Sometimes τ is called the "one over e " time. Although the half-life is almost always used to describe the decay rate of radioactive elements, it is common for chemists to talk about the rate of first order processes in chemistry in terms of the relaxation time.

Kinetics

Kinetics is the area of chemistry concerned with reaction rates. The rate can be expressed as:

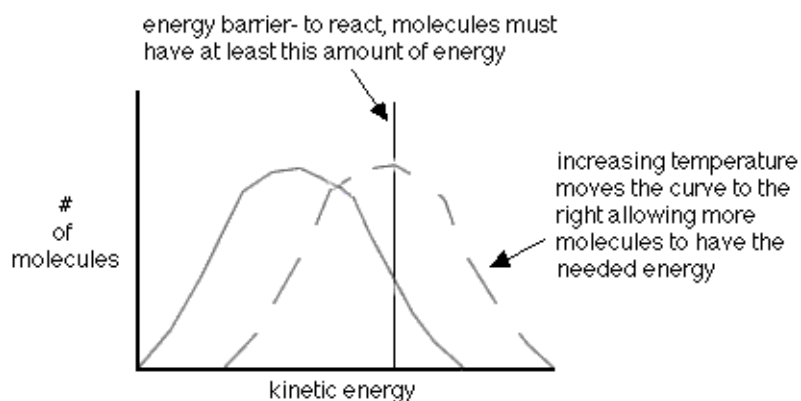
rate = change in substance/time for change to occur (usually in M/s)

There are several factors that determine the rate of a specific reaction and those are expressed in the "collision theory" that states that for molecules to react, they must:

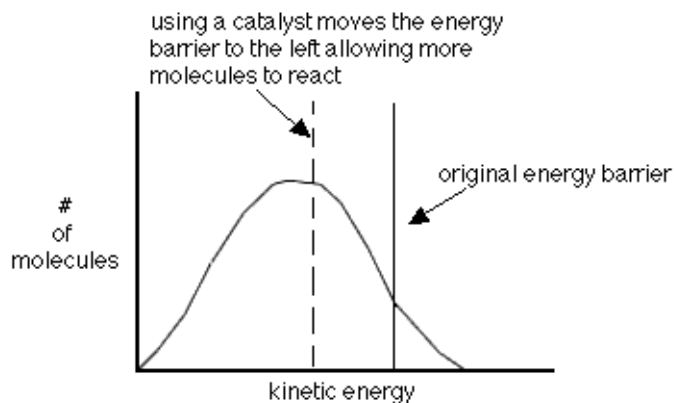
- collide
- have the right energy
- have the right geometry

To increase the rate, you must make the above more likely to occur. This is possible by changing other factors such as:

- increasing the surface area (of solids)-this allows for more collisions and gives more molecules the right geometry
- increasing the temperature-this gives more molecules the right energy (also called the activation energy, E_a)



- increasing the [concentration](#) (of gases and solutions)-this allows for more collisions and more correct geometry
- using a [catalyst](#)-helps molecules achieve the correct geometry by providing a different way to react



The reaction rate can also be expressed by using a "rate law" and is written as follows:

For the general reaction: $aA + bB + \dots \rightarrow gG + hH + \dots$

the reaction rate can be calculated by:

$$\text{Reaction rate} = k[A]^m[B]^n \dots$$

Where:

[A], [B], etc. are the concentrations of the [reactants](#)

k is the rate constant or rate coefficient, a value dependent on temperature.

m,n, etc. are exponents that correspond to **a, b**, etc. The concentration is raised to the power of its coefficient in the balanced equation.

Reaction order is a topic that comes with reaction rates. If you have a reaction in that A, B, and C are possible reactants, then we can describe the order of the reaction following this chart:

$$\text{Rate} = kC_a \quad \text{1st order}$$

$$\text{Rate} = kC_a^2 \text{ or } kC_a C_b \quad \text{2nd order}$$

$$\text{Rate} = kC_a^3 \text{ or } kC_a C_b C_c \quad \text{3rd order}$$

The order of the reaction is defined as the sum of the exponents of the coefficients. In general, first order reactions are most commonly seen, but reactions of other orders are also important. Zero-order reactions -- those for that the change in the reaction is independent of the concentration of the reaction -- are also possible.

It is possible to determine the order of a reactant, and eventually the reaction rate, using initial rate information that includes the concentration of the reactants and the rate at that the product is formed. If you double the concentration of reactant X and the rate increases by 2^a , then the order of reactant X is "a". If you triple the concentration of reactant Y and the rate increases by 3^b , then the order of Y is "b". For example, if you have a reaction with one reactant, A, and you double [A] and the rate doubles, then the rate $= k[A]^1$. If, instead, you double [A] and the rate quadruples, the rate $= k[A]^2$. If you double [A] and the rate stays the same, then the rate $= k[A]^0$.

To find the rate constant, k, using initial rate information, just plug in from the experiment one of the concentrations and rate into the rate law and solve. The units of k are trickier:

$$\text{units of } k = \text{units of rate} / (\text{units of concentration})^{\text{reaction order}}$$

$$\text{Ex: for 2nd order reaction, } k = (\text{M/s}) / \text{M}^2 = \text{M}^{-1} \text{s}^{-1}$$

Example Problem: Find the rate law and rate constant of $A + B \rightarrow C$ using the following data

Ex #	[A] (M)	[B] (M)	initial rate of C (M/s)
1	.100	.100	4.0×10^{-5}
2	.100	.200	4.0×10^{-5}
3	.300	.100	3.6×10^{-4}

Answer: doubling [B] had no effect on the rate so B is zero order

tripling [A] caused the rate to multiply by 9 or by 3^2 , so A is 2nd order.

$$\text{rate} = k[A]^2 [B]^0 = k[A]^2$$

$$4.0 \times 10^{-5} = k(.100)^2 \quad k = 4.0 \times 10^{-3} \text{ M}^{-1} \text{s}^{-1}$$

When dealing with reaction rates, it is sometimes important to know how to graph a straight line with the data you have. When graphing concentration versus time, there are two ways to graph a line. If you have a first order reaction, then the graph of $\ln[A]$ vs. time is a line. If you have a second order reaction, then the graph of $1/[A]$ vs. time produces a line.

A quantitative way to examine reaction rates is through **Arrhenius Equation** that states:

$$k = Ae^{-E_a/RT}$$

Where:

A is a constant related to the geometry needed

e is a constant, approximately 2.7281

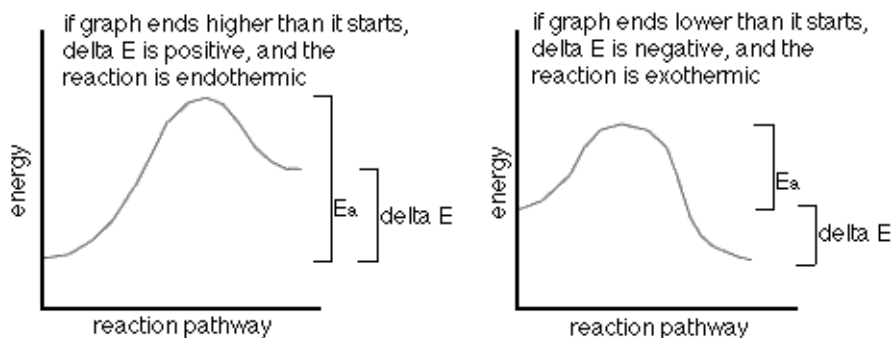
E_a is the activation energy

R is the gas law constant, 8.314 J/mol-K

T is the temperature in kelvins

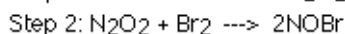
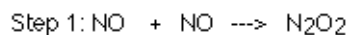
If it is a simple geometry to attain, A will be large. If a large E_a is needed then the exponent becomes more negative and therefore decreases k. If the temperature increases then the exponent becomes less negative and therefore increases k. A [pop-up calculator](#) is available to help practice using Arrhenius' Equation to make calculations.

The following are two (2) energy profile graphs that help demonstrate energy changes during a reaction.

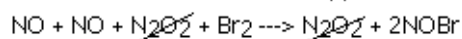


Not all reactions happen exactly as they are written. Most, in fact, go through an intermediate step. **Reaction mechanism** studies look at how a reaction actually occurs. Defined, a reaction mechanism is a series of elementary reactions that are proposed to account for the rate law (kinetics) of a particular reaction. The diagram below shows the two steps involved in a particular mechanism, and it shows how we get the reaction from the mechanism.

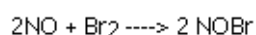
mechanism:



Now we add up all the terms on both sides of the reaction and cancel out those that appear on both sides.



reaction:



It is helpful to remember certain terms and facts when dealing with mechanisms. You cannot derive a mechanism from the equation and when you combine the steps of a mechanism, you end up with the reaction. The molecularity of a step tells how many molecules are involved (most involve two (2) molecules so they are bimolecular). An intermediate product is a molecule formed in one step and then used in another. One of

the most important concepts to keep in mind is that the steps are not equally important. To speed up the reaction, you must speed up the slowest step (also called the rate-determining step).

rate law of slow step = rate law of reaction

When determining the rate of a step, simply make the exponent of the reactant's concentration in the rate law the same as the coefficient of the reactant in the step.

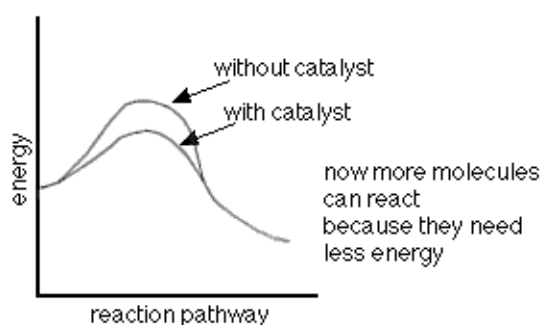
Example problem: Find the slow step of the following reaction mechanism

reaction : $2\text{NO} + \text{Br}_2 \rightarrow 2\text{NOBr}$
 mechanism: step 1) $\text{NO} + \text{NO} \rightarrow \text{N}_2\text{O}_2$
 step 2) $\text{N}_2\text{O}_2 + \text{Br}_2 \rightarrow 2\text{NOBr}$

Ex #	[NO] (M)	[Br ₂] (M)	initial rate of NOBr (M/s)
1	.10	.10	.040
2	.10	.20	.080
3	.20	.20	.320

Answer : doubling [Br₂] doubles rate so B is first order and doubling [NO] and [Br₂] multiplies the rate by 8 or 2³ so NO is second order
 the observed rate = $k[\text{Br}_2][\text{NO}]^2$
 rate of step 1 = $k[\text{NO}][\text{NO}] = k[\text{NO}]^2$
 rate of step 2 = $k[\text{N}_2\text{O}_2][\text{Br}_2] = k[\text{NO}]^2[\text{Br}_2]$
 N₂O₂ isn't a reactant so you must split it into its components
 Step 2 is the slow step because its rate agrees with the observed rate

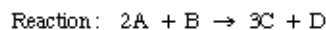
A **catalyst** is a substance added to a reaction that comes out of the reaction unchanged. As mentioned earlier, catalysts help lower the activation energy as shown in the following graph. They do this by changing the reaction mechanism.



The following is an example of how this can be done.

reaction without catalyst : $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$
 this is a one -step reaction
 reaction with catalyst : $2\text{H}_2\text{O}_2 \xrightarrow{\text{Br}_2} 2\text{H}_2\text{O} + \text{O}_2$
 the Br₂ allows this to be a two -step reaction
 1. $\text{H}_2\text{O}_2 + \text{Br}_2 \rightarrow 2\text{Br}^\cdot + 2\text{H}^\cdot + \text{O}_2$
 2. $\text{H}_2\text{O}_2 + 2\text{Br}^\cdot + 2\text{H}^\cdot \rightarrow \text{Br}_2 + 2\text{H}_2\text{O}$
 this two -step reaction is faster than the one -step reaction

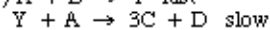
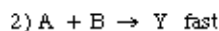
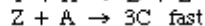
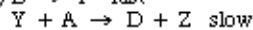
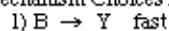
Practice Kinetic Quantitative Problem:



Initial Rate Information :

Ex #	[A] (M)	[B] (M)	Rate (M / hr)
1	.240	.120	2.00
2	.120	.120	.500
3	.240	.0600	1.00
4	.0140	.135	?

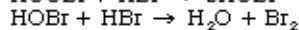
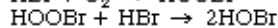
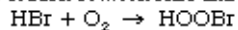
Mechanism Choices:



- Write the rate law expression .
- Calculate k with units .
- Calculate the rate for experiment 4.
- What is the final [C] for experiment 1.
- Select the best mechanism and explain .

Practice Kinetic Qualitative Problems:

The reaction between HBr and O_2 is believed to occur in 3 steps:



- Write a balanced equation for the overall reaction
- Identify the intermediates .
- From the mechanism, the rate = $k[HBr][O_2]$. Which is the rate - determining step?
- Why does increasing temperature increase k?